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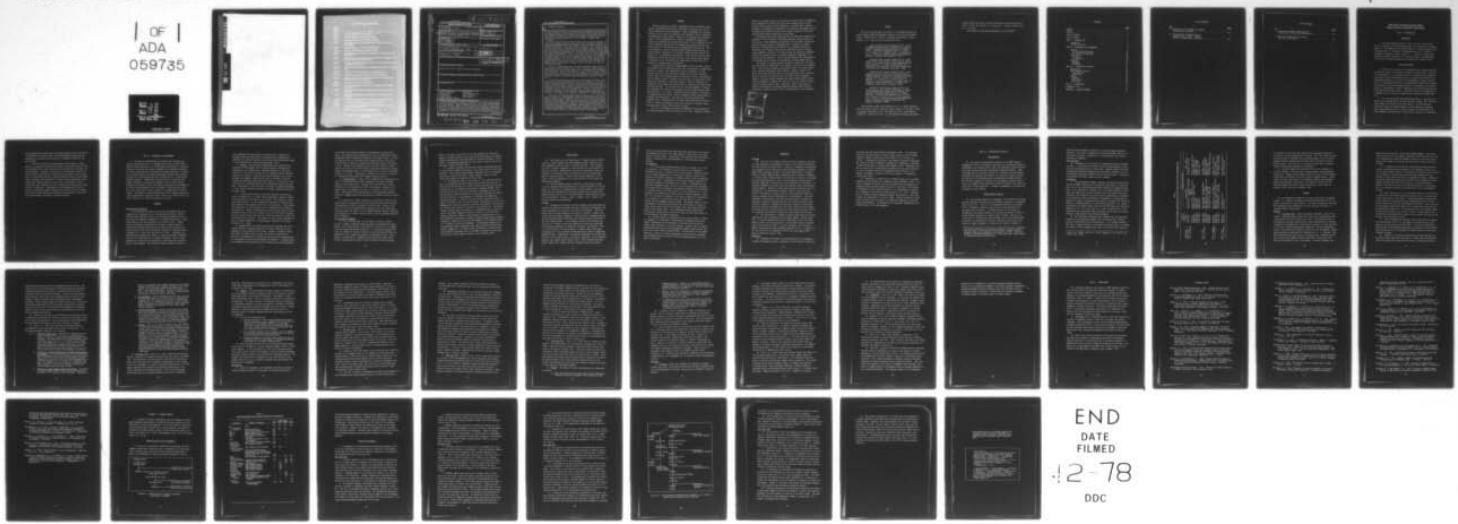
ARMY ENGINEER WATERWAYS EXPERIMENT STATION VICKSBURG MISS F/G 13/2  
WATER QUALITY IMPACTS OF AQUATIC DREDGED MATERIAL DISPOSAL (LAB--ETC(U))  
AUG 78 S A BURKS, R M ENGLER

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20. ABSTRACT (Continued).

material and then deposited on the bottom when the suspended material settles. The time necessary to achieve the equilibrium condition depends upon the physicochemical conditions in the aquatic system and the quantity and duration of the contaminant introduction. There has been concern that dredging and open-water disposal operations may release these trapped contaminants to the overlying water column again and thus have the potential to damage aquatic environments.

Dredged Material Research Program (DMRP) reports and other literature indicate that dredging operations have the potential to temporarily mobilize or release some contaminants from the sediments. During disposal operations, the anaerobic sediments are mixed with aerated surface water, and a complex chemical interaction occurs. Heavy metals, such as cadmium, copper, chromium, lead, and zinc, are stabilized in the oxygen-free sediments as insoluble sulfides. When the sediments are oxygenated, these metals form oxides that are slightly more soluble than the metal sulfides. The reduced forms of iron and manganese in oxygen-free sediments are, however, more soluble than the oxides formed in the overlying water. As a result, immediately after disposal of sediments in oxygenated surface waters, iron and manganese hydrous oxides begin to coagulate and precipitate. The surface of the iron hydrous oxide coagulates has a strong affinity for other heavy metals and effectively sorbs or removes the slightly soluble metal oxides of cadmium, copper, chromium, lead, and zinc from the water column.

The cycle of phosphorus between the oxygenated surface waters and the reduced sediment closely parallels that of iron. Therefore, during disposal of dredged material in open waters, soluble forms of phosphorus may be temporarily released until they are scavenged from the water column by ferric hydrous oxide coagulates. The other major nutrient, nitrogen, is accumulated in sediments in the reduced form ammonia, which is highly water soluble and thus can be readily released to the water column during disposal operations in open water.

Chlorinated hydrocarbon pesticides and oil and grease compounds in sediments are not released in significant amounts during disposal in open waters. These compounds are generally not very water soluble and thus are rapidly sorbed by suspended solids. Disposal of dredged material containing high concentrations of chlorinated hydrocarbon pesticides will probably not cause any significant effects on water column organisms. However, the pesticide and oil and grease compounds could have an adverse effect on benthic organisms attempting to recolonize the new sediments. These potential impacts were investigated in the DMRP and the results are synthesized in another DMRP report.

The effects of dredged material disposal in open water are temporary and primarily restricted to the immediate vicinity of the disposal area. Toxic levels of ammonia, and possibly some of the heavy metals, may be released immediately after disposal. However, within a few hours, the levels of metals should be decreased below toxic concentrations by dilution and sorption onto iron hydrous oxide coagulates. Ammonia is usually rapidly reduced below toxic concentrations by dilution; biooxidation of ammonia may also occur but is a slower process, usually requiring several days. Therefore, careful monitoring of ammonia concentrations at dredged material disposal sites should be performed to prevent buildup of toxic concentrations of this compound.

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## SUMMARY

Natural processes in aquatic ecosystems tend to concentrate heavy metals, chlorinated hydrocarbons, pesticides, nutrients, and oil and grease compounds in bottom sediments. These contaminants are not very soluble in water under the conditions that normally occur in oxygenated uncontaminated surface waters. Therefore, introducing high concentrations of these contaminants into aquatic ecosystems will generally result in an equilibrium condition where most of the contaminant will be sorbed (adsorbed and absorbed) by suspended particulate material and then deposited on the bottom when the suspended material settles. The time necessary to achieve the equilibrium condition depends upon the physicochemical conditions in the aquatic system and the quantity and duration of the contaminant introduction. There has been concern that dredging and open-water disposal operations may release these trapped contaminants to the overlying water column again and thus have the potential to damage aquatic environments.

Dredged Material Research Program (DMRP) reports and other literature indicate that dredging operations have the potential to temporarily mobilize or release some contaminants from the sediments. During disposal operations, the anaerobic sediments are mixed with aerated surface water, and a complex chemical interaction occurs. Heavy metals, such as cadmium, copper, chromium, lead, and zinc, are stabilized in the oxygen-free sediments as insoluble sulfides. When the sediments are oxygenated, these metals form oxides that are slightly more soluble than the metal sulfides. The reduced forms of iron and manganese in oxygen-free sediments are, however, more soluble than the oxides formed in the overlying water. As a result, immediately after disposal of sediments in oxygenated surface waters, iron and manganese hydrous oxides begin to coagulate and precipitate. The surface of the iron hydrous oxide coagulates has a strong affinity for other heavy metals and effectively sorbs or removes the slightly soluble metal oxides of cadmium, copper, chromium, lead, and zinc from the water column.

The cycle of phosphorus between the oxygenated surface waters and the reduced sediment closely parallels that of iron. Therefore, during

disposal of dredged material in open waters, soluble forms of phosphorus may be temporarily released until they are scavenged from the water column by ferric hydrous oxide coagulates. The other major nutrient, nitrogen, is accumulated in sediments in the reduced form ammonia, which is highly water soluble and thus can be readily released to the water column during disposal operations in open water.

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## PREFACE

This report synthesizes the results of the Dredged Material Research Program (DMRP) Environmental Impacts and Criteria Development Project (EICDP) Task 1C, Effects of Dredging and Disposal on Water Quality. It is based on the following work units:

Work Unit 1C03, Contract Report D-76-7: Effect of Sediment Organic Matter on Migration of Various Chemical Constituents During Disposal of Dredged Material. Principal investigators were B. E. Blom, T. F. Jenkins, D. C. Leggett, and R. P. Murrmann of the U. S. Army Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire 03755.

Work Unit 1C04, Contract Report D-75-6: Laboratory Study of the Release of Pesticide and PCB Materials to the Water Column During Dredging and Disposal Operations. Principal investigators were Richard Fulk, David Gruber, and Richard Wullschleger of Envirex, Inc., Milwaukee, Wisconsin 53201.

Work Unit 1C05, Contract Report D-77-4: Transformations of Heavy Metals and Plant Nutrients in Dredged Sediments as Affected by Oxidation-Reduction Potential and pH. Principal investigators were R. P. Gambrell, R. A. Khalid, M. G. Verloo, and W. H. Patrick, Jr., of the Laboratory of Flooded Soils and Sediments, Agronomy Department, Louisiana State University, Baton Rouge, Louisiana 70803.

Work Unit 1C06, Contract Report D-76-1: Research Study on the Effect of Dispersion, Settling, and Resedimentation on Migration of Chemical Constituents During Open-Water Disposal of Dredged Material. Principal investigators were K. Y. Chen, S. K. Gupta, A. Z. Sycip, J. C. S. Lu, M. Knezevic, and W. S. Choi of the Environmental Engineering Program, University of Southern California, Los Angeles, California 90007.

This synthesis report was prepared by Dr. S. A. Burks, Oklahoma State University, and Dr. Robert M. Engler, Manager of the EICDP, under the general supervision of Dr. John Harrison, Chief, Environmental Laboratory. Directors of the U. S. Army Engineer Waterways Experiment

Station during the period of report preparation and publication were COL G. H. Hilt, CE, and COL J. L. Cannon, CE. Technical Director was Mr. F. R. Brown.

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WATER QUALITY IMPACTS OF AQUATIC DREDGED  
MATERIAL DISPOSAL (LABORATORY INVESTIGATIONS)

PART I: INTRODUCTION

Background

1. The work synthesized herein is only one part of an overall effort to determine the environmental impact of the disposal of dredged material. These DMRP efforts included Tasks 1A - Aquatic Disposal Field Investigations, 1B - Movements of Dredged Material, 1C - Effects of Dredging and Disposal on Water Quality, 1D - Effects of Dredging and Disposal on Aquatic Organisms, 1E - Pollution Status of Dredged Material, and 2D - Confined Disposal Area Effluent and Leachate Control.

Purpose and Scope

2. Within the overall scope of dredged material disposal research, the work on effects of dredging and disposal on water quality (Task 1C) is interrelated to the five other tasks by providing data on conditions under which various contaminants could be released from sediments; by establishing guidance for selection and management of aquatic disposal sites; by providing information for determining the spatial and temporal distribution of disposed dredged material; by determining the potential impact of contaminants on aquatic organisms; and by interacting with the Environmental Protection Agency to establish criteria and guidelines on a regional basis to assist in regulating the disposal of dredged material.

3. Five work units were performed within Task 1C. One work unit (1C01) was a planning effort, and the other four (1C03, 1C04, 1C05, and 1C06) formed the nucleus of the Task research. The work involved laboratory studies of bottom sediments from representative dredging areas along Atlantic, Pacific, and Gulf coasts, the Great Lakes, and some freshwater riverine areas. This work was carried out to determine

what contaminants are mobilized or released during disposal; how much of a contaminant is released; under what physicochemical conditions contaminants are released; and how long the contaminants persist in the water column.

4. While the laboratory investigations were designed to answer many of the questions concerning the impact of open-water disposal, they could simulate only a small fraction of the possibilities that occur in real situations. Therefore, the results of the laboratory studies can only be used as guidelines for predicting the potential effects of disposal at field sites; because of limited dilution (which is usually much higher in nature) and the ability to closely control and monitor conditions, these studies represent only worst-case simulations. Field studies were also conducted to test the laboratory results under a wider variety of conditions. Consequently, these findings must be used to predict the expected boundary conditions and should be used in conjunction with the field studies and biological evaluations for a more complete understanding of potential ecological impacts.

## PART II: BACKGROUND AND ASSESSMENT

5. The state-of-the-knowledge of sediment and soil-water geochemical interactions prior to the DMRP was such that certain fundamental concepts relating to the transformation and release or retention of metals, nutrients, and organic compounds were adequately developed but had not been applied to dredging and disposal operations. Moreover, little work had dealt with highly contaminated sediment-water systems and those few investigations had been inconclusive as to related environmental impacts. Consequently, selected items of literature that present significant concepts were reviewed for this report and are presented in this part to give the reader a background and assessment of the state-of-the-knowledge prior to the DMRP. This literature represents only a small part of that reviewed in the DMRP Task 1C contract reports. The reader is referred especially to the following reports for a more comprehensive literature review: Blom et al. (1976), Fulk et al. (1975), Khalid et al. (1977), and Chen et al. (1976).

### Organics

#### Chlorinated hydrocarbons

6. Chlorinated hydrocarbons such as DDT and dieldrin and other organochlorine compounds such as polychlorinated biphenyls (PCB's), polychlorinated terphenyls (PCT), and chlorinated dibenzodioxins are notorious environmental contaminants of worldwide significance. These constituents do not exist naturally in the earth's crust. Organochlorine compounds are generally not soluble in surface waters at concentrations higher than 20 parts per billion ( $\mu\text{g/l}$ ) and most are found associated with either biological organisms or suspended solids (Freedman et al., 1953, and Poirrier et al., 1972). Therefore, the organochlorine compounds not taken up by aquatic organisms eventually settle to the bottom deposits in aquatic ecosystems. Most of these compounds are stable and may accumulate to relatively high concentrations in the sediments. The manufacture and/or disposal of most of

these compounds has been stopped by Federal action. However, the sediments that have already been contaminated with organochlorine compounds will probably continue to have potentially deleterious levels of these compounds for several decades (Dennis, 1975).

7. Release. When sediments contaminated with organochlorine compounds are resuspended, such as during hydraulic dredging, will a percentage of the organochlorine compounds redissolve in the water column or is the sorption affinity for the sediments greater than the potential for release? Clay particles are an important part of most sediments and possess a large surface area for sorption of various constituents including heavy metals and organics. The surface of clay particles may be highly modified by the surrounding chemical environment. Furthermore, it has been shown in studies of pesticide movements in soils that clay particles tightly sorb organic compounds (White and Mortland, 1970).

8. In percolation studies of pesticide migration through loam soils, Lichtenstein et al. (1967) found no measurable amounts of aldrin in the percolation water from the soil column. Small amounts of para-thion were detected. It was concluded that migration of pesticides in soils depends on the aqueous solubility of the pesticide. Other studies have shown that the total volume of water flushing the soil columns is also important. Biggar (1970) showed that the leaching volume of water required to reduce 1.05 µg of lindane in one inch of soil by 50 percent was 20.7 inches of water and that 39.6 inches was required to reduce the concentration by 90 percent. The presence of other organic compounds in soils is highly influential in determining the release of pesticides (Wershaw et al., 1969).

9. Organochlorine (chlorinated hydrocarbon) compounds tend to be readily sorbed by suspended solids with low water solubility of the compounds in the parts-per-billion range. However, information available before the DMRP could not answer the question concerning the potential resolubilization of pesticides associated with sediments that are resuspended, such as during dredging and disposal. It appeared that the organochlorine compounds tend to be released until some equilibrium

concentration was achieved between the aqueous phase and the solid phase. The organochlorine compounds would then be readsorbed by other suspended solids or biological organisms in the water column. It could be predicted that the concentration of organochlorines in the water column would be reduced to nondetectable quantities within a few hours or less. Studies of PCB migration in the Southern California Bight indicate that most of the PCB's found in municipal effluents are rapidly sorbed and sedimented within a few kilometres of the point of discharge (Young et al., 1976). Consequently, sediments are a sink or reservoir for chlorinated hydrocarbons with unknown release potential.

10. Concentrations. Dennis (1975) summarized the concentration of PCB's in surface waters and bottom sediments of the major drainage basins of the United States. Analyses since 1971 indicate a slight reduction in the concentration of PCB's in sediments. However, it is expected that the sediments will act as a reservoir of PCB's for decades. This reservoir has the potential for environmentally harmful effects as dredging operations and open-water disposal continue in these areas.

11. Young et al. (1976), reporting on the inputs of PCB's to the coastal waters off southern California, found that there were considerable quantities of PCB's discharged to the bay areas. However, very little of this PCB contamination was detected in the open ocean, thus indicating again that PCB's are not transported under natural conditions long distances in a soluble form but tend to sorb to suspended materials and to sediments.

#### Oil and grease compounds

12. The collective term "oil and grease" includes a complex variety of organic compounds composed primarily of hydrogen and carbon. However, this review focuses on the effects of crude oil or oil pumped from subterranean geological formations. It has been established that crude oil spilled on the water surface will be distributed between the atmosphere, water column, and sediments (Nelson-Smith, 1973). Consequently, oil deposited in sediments should contain the least water-soluble compounds and the least volatile fractions from the original

mixture. Microbial action upon oil in the sediments will generally degrade the normal aliphatics (straight-chain hydrocarbons) and simpler aromatics (benzene-ring type hydrocarbons) (Shelton and Hunter, 1975); however, the remaining compounds from the crude oil mixture may be very persistant (Blumer and Sass, 1972).

13. Studies of benthic and intertidal marine organisms exposed to a crude oil spill indicate that most of the effects occur shortly after the spill. Most benthic and intertidal organisms return to a prespill state after a year or two (North, 1967); however, effects on some species may persist for many years (North, 1974).

14. An excellent review of the effects of oil on marine environments cited numerous articles dealing with the short-term effects of crude oil spills but only two or three studies concerned with the long-term effects of oily sediments upon aquatic organisms (GESAMP, 1977). The fate and effect of heavy oil fractions in sediments are not adequately known to make any definitive predictions concerning the effect upon water quality of resuspending oily sediments by dredging and disposal operations. Inferences derived from the laboratory study of Shelton and Hunter (1975) are that anaerobic decomposition of oil in the sediments will reduce the partially oxidized and aliphatic fractions but not the more toxic aromatic fractions of the original oil. The aromatic fraction contains some of the more toxic compounds found in crude oil, such as the simple aromatics (benzene, toluene, etc.) and the more complex polynuclear aromatics (benz(a)pyrene, benzanthracene, etc.). The probability of polynuclear aromatic compounds persisting in aquatic sediments is supported by Strosher and Hodgson's (1975) identification of 27 compounds in Lake Erie sediments. Resuspending sediments containing these aromatic compounds could cause deleterious effects upon aquatic communities. The extent would be difficult to predict based upon scientific knowledge prior to the DMRP, although the indications are that the overall impact is likely to be relatively small.

### Heavy Metals

15. The collective term "heavy metals" is widely used to describe a group of common elements including cadmium, copper, chromium, iron, lead, manganese, mercury, nickel, selenium, and zinc. These elements are toxic to aquatic organisms at concentrations of soluble material of parts per million or substantially less and are relatively common contaminants in both point source and nonpoint sources of surface water input to receiving waters. They are also natural components of the earth's crust and subsequently are always present in both dredged and undisturbed sediments.

16. The environmental impact potential of heavy metals is made even more complex because some metals are required nutrients by all life forms. On the basis of estimated inputs of heavy metals to the world's oceans over the concentration that poses minimal risk, Ketchum (1975) ranked the toxic metals in the following order of their potential hazard to the environment: mercury > nickel > cadmium > zinc > copper, with mercury ranked the most hazardous.

#### In water

17. Dissolved heavy metals also form complexes with many materials such as the hydroxides, sulfides, sulfates, chlorides, bicarbonates, and other constituents in solution in the aquatic environment. These complexes limit the bioavailability and toxicity of metals. Metals occur as free ions and organic complexes in natural waters, depending upon the existing physicochemical conditions, and in these forms are more available for organism impact. As an example, Gardiner (1974) showed that from 35 to 71 percent of the total cadmium in solution was associated with inorganic complexes of carbonates, chlorides, and sulfates. Only 1.6 to 6.9 percent of the total amount of nickel, cobalt, and copper transported in a river occurred as dissolved and/or soluble organically complexed forms. Consequently, the greatest percentage of the metal was found in the less mobile form of crystalline particles, surface adsorbed material, and organic solids (Gibbs, 1973). These studies, plus many others, support the concept that most inorganic forms of the heavy

metals are poorly soluble and form solid phase materials or are sorbed by suspended material at the normal ranges of pH and redox potentials found in surface waters. Consequently, the potential for water quality impact is limited by the physicochemistry of the particular aquatic systems.

In sediments

18. Since bottom sediments generally have no oxygen (i.e., they are anaerobic), the chemistry of heavy metals in the sediments is different from that in oxygen-rich or aerated waters. Microbial breakdown of organic substances in the anaerobic sediments results in the formation of sulfides, ammonia, and reduced forms of iron and manganese (Hutchinson, 1957). Subsequently, heavy metals normally stabilize in anaerobic sediments as insoluble metal sulfides. When sediments are mixed with oxygenated water, such as occurs during hydraulic dredging, the sulfides will be oxidized with subsequent oxidation of heavy metals. The oxidized forms of the heavy metals, with the exception of iron and manganese, are somewhat more soluble than the sulfide compounds. However, the increase in solubility of the metal oxides may be compensated for by sorption of trace metal cations onto the surface of poorly soluble iron and manganese hydrous oxides. The hydrous oxides of iron and manganese form colloidal particles that precipitate and exhibit a large, active surface area that scavenges other trace metals from the water column (Jenne, 1968). This scavenging process significantly restricts the availability of metals and tends to limit their impact on bottom sediments and benthic organisms.

19. Briefly stated, the potentially active heavy metals in anaerobic sediments are stabilized or immobilized as insoluble sulfide compounds. Resuspension of the sediments in aerated surface waters may release small quantities of the toxic metals. However, they are rapidly removed from solution by iron and manganese hydrous oxides and may form many other poorly soluble oxidized forms. Interpretation of the release potential of metals is further complicated by the fact that uncontaminated sediments and water contain various concentrations of all of the metals in question.

## Nutrients

### Nitrogen

20. The cycle of nitrogen in natural waters, sediments, and soils has been intensively investigated and much of the existing information has been reviewed by Keeney (1973). Generally, atmospheric nitrogen gas ( $N_2$ ) undergoes cyclic reduction by some biological organisms to organic amines ( $NH_2^-$ ) (nitrogen fixation), microbial decomposition of organic amines to release ammonia ( $NH_3$ ) (mineralization), oxidation of ammonia to nitrates ( $NO_3^-$ ) (nitrification), and reduction of nitrates to nitrogen gas ( $N_2$ ) (denitrification). Most of these reactions are mediated by microbial organisms in response to the availability of free oxygen. In anaerobic sediments, microbial activities degrade organic detritus and release ammonia. Ammonia is stable under anaerobic conditions and can accumulate in the interstitial sediment waters to relatively high levels. The quantity of ammonia found in the interstitial waters depends upon organic matter concentration in the sediments. Therefore, sediments in water bodies receiving large quantities of organic contaminants, especially municipal wastes, will contain elevated concentrations of ammonia. Dredging and open-water disposal of these sediments may disperse the ammonia into the water column and water column concentrations may reach toxic levels for many forms of aquatic life if not dissipated and diluted by mixing with large quantities of water.

21. The concentration of ammonia lethal to many species of aquatic organisms has been determined with un-ionized ammonia, the most toxic form. In aquatic systems there will be 1800 times as much un-ionized ammonia present at pH 8 than at pH 6. The pH range in most uncontaminated surface waters is from 7 to 8 and, therefore, the un-ionized ammonia concentrations would probably range from 0.12 to 1.2 percent at  $5^\circ C$  and from 0.8 to 7.5 percent at  $30^\circ C$  of the total ammonia (EPA Quality Criteria for Water, 1976).

### Phosphorus

22. Phosphorus is probably the most essential of all elements to biological organisms and thus a deficiency is more likely to limit pro-

ductivity than any other material (Hutchinson, 1957). The concentrations of total phosphorus in natural surface waters of lakes in humid temperate regions is generally in the range of 10 to 40 parts per billion. Contamination principally from domestic wastewater discharges may elevate the total phosphorus concentration considerably, resulting in excessive growths of nuisance algae (Sawyer, 1946). Phosphorus is of little concern from a toxicological standpoint but can cause overfertilization of natural waters with subsequent harmful effects to the aquatic ecosystems. A complete review of the subject is presented by Vollenweider (1970).

23. Phosphorus in surface water is rapidly taken up by biological organisms and by sorption onto suspended solids (Schindler, 1971). As a result, sediments accumulate elevated concentrations of phosphorus as suspended solids and dead organisms settle to the bottom. The release of phosphorus from the sediments appears to be interrelated to that of iron, manganese, and possibly aluminum (Syers et al., 1973). Resuspension of sediments during dredging operations and disposal in open water releases the phosphorus to the water column. However, Mudroch and Cheam (1974) reported that the quantity of phosphorus remaining in the water column was negligible. The phosphorus was apparently readsorbed by the oxidized forms of iron and manganese.

### PART III: DISCUSSION OF RESULTS

#### Introduction

24. The state-of-the-knowledge presented in pre-DMRP research (summarized in Part II) suggested conditions that may enhance release of contaminants from sediments while there were geochemical conditions that may retard release and render contaminated sediments harmless. DMRP investigations were therefore carried out to determine the geochemical conditions that maximize and minimize the release of organics, metals, and nutrients from contaminated and noncontaminated dredged material. This work was conducted to evaluate the environmental effects under a variety of sediment-water conditions as well as present "worst case" and "best case" release conditions. A number of geographical locations are represented in the studies.

#### DMRP Research, Task 1C

25. The methods summarized in Appendix A deal primarily with those general procedures that were used by the DMRP contractors to accomplish Task 1C work units. There are no standardized methods for fractionation\* of sediments; therefore, each contractor was responsible for developing test procedures. The DMRP assisted the contractors in designing of the general sediment fractionation procedures in order to obtain maximum comparability between each of studies. However, the contractors, in collaboration with the DMRP, had to develop additional procedures for obtaining more specific fractions such as metals complexed by organic compounds or fractions that might be released at

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\* Fractionation refers to the selective chemical extraction procedures that were used to differentiate the partitions or phases within a sediment where various chemical constituents are found. The partitioning or sediment distribution of a constituent has a direct effect on its mobility and bioavailability.

specific physical-chemical conditions of pH and oxidation-reduction potential. The reader is referred to the pertinent DMRP reports\* for more specific details. Summaries of the methodologies are, however, presented in Appendix A.

Site selection

26. Sampling sites, locations, and characteristics are presented in Table 1. The sites were selected to give broad geographical variation and wide applicability to other areas. Samples ranged from highly contaminated freshwater sediments from the Detroit, Michigan, area to uncontaminated estuarine sediments from a Louisiana marsh. Locations on the Atlantic and Pacific coasts were also sampled.

Limitations

27. The experimental designs, sampling, and analytical procedures used by the DMRP contractors were laboratory simulations of conditions that occur in the field during open-water disposal of dredged material. Since it was impossible to simulate all of the physical-chemical conditions that might occur in field disposal sites, the results that were obtained in the laboratory can only be used as guidelines or boundaries for estimating be used as guidelines or boundaries for estimating the quantity of chemical constituents that might be released from open-water disposal of dredged material in actual field situations. The complex fractionation procedures used by the 1C05 and 1C06 work unit contractors (Gambrell et al., 1977, and Chen et al., 1976) illustrate part of the complicated and interrelated physical-chemical factors that can affect release of constituents from disturbed sediments.

28. The limitations discussed above indicate that the laboratory results may not completely simulate field conditions and, therefore, should be confirmed by field investigations. It is thought, however, that due to limited dilution in the laboratory and the ability to sample and analyze discrete sediment-water zones or interfaces that cannot be

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\* Blom et al. (1976), Fulk et al. (1975), Gambrell et al. (1977), and Chen et al. (1976).

**Table 1**  
**Location of Sediment Sampling Sites of the Task 1C Work Unit Investigations**

Work Unit	Type of Collection Site	Sampling Locations	
		Water Body	City, State
1C03 - Blom et al. (1976)	Estuarine	Hudson River - Edgewater Weehawken Channel	Manhattan, New York
	Estuarine	Passaic River - Shooter's Island	Staten Island, New York
	Fresh water	Hudson River - Newton Creek	Brooklyn, New York
	Fresh water	Saginaw River	Saginaw, Michigan
	Fresh water	Rouge River	Detroit, Michigan
		Maumee River	Toledo, Ohio
1C04 - Fulk et al. (1975)	Fresh water	Lake Michigan - Calumet Harbor	Chicago, Illinois
	Fresh water	Lake Superior - Fox River	Green Bay, Wisconsin
	Fresh water	Mississippi River - Memphis Harbor	Memphis, Tennessee
	Estuarine	Galveston Bay - Tabbs Bay	Houston, Texas
	Estuarine	Fall River - Mt. Hope Bay	Fall River, Massachusetts
1C05 - Gambrell et al. (1977)	Estuarine	Barataria Bay - Bay Ronfleur	Grand Isle, Louisiana
	Estuarine	Mobile Bay - South of Pinto Island	Mobile, Alabama
	Fresh water	Mississippi River - Mile 88	New Orleans, Louisiana
	Fresh water	Calcasieu River - Prier Lake	Lake Charles, Louisiana
1C06 - Chen et al. (1976)	Estuarine	Los Angeles Harbor	Los Angeles, California
	Fresh water	Morris Dam	Azusa, California

be evaluated in the field, the laboratory investigations represent a "worst case" for many parameters of interest. The "worst case" approach can then be used to estimate worst extremes possible in the field and separate inactive constituents from those with a potential for water quality impact. Thus, the use of the results should lead to environmentally conservative guidelines or boundaries.

29. The most significant limitation is due to an inability to directly estimate or predict aquatic organism impact from geochemical evaluations. Neither soluble phase analysis nor total or bulk sediment concentration evaluations can clearly predict organism impact. Consequently one must rely primarily on biological studies and complement these with geochemical evaluations. The reader is referred to the Synthesis Reports for Task 1D (Disalvo and Hirsch, 1978), Task 1E (Brannon, 1978), and Task 1H (Wright, 1978).

### Results

30. This discussion integrates the major conclusions by chemical groups, i.e., organics (including chlorinated hydrocarbons and oil and grease), heavy metals, and nutrients. The results included are the ones most significant when attempting to predict the fate and effect of sediment chemical constituents.

#### Organics

31. Work Unit 1C04. Envirex performed a laboratory study of the release of pesticide and PCB materials to the water column during simulated disposal operations (Fulk et al, 1975). The objectives were to determine the type and concentration of pesticide materials in selected sediments to be dredged and to determine the transfer of these materials to the water column during disposal operations. The most significant result of this study was detection of PCB's in 59 of 64 samples, clearly demonstrating the widespread PCB contamination of U. S. waterways. The PCB's identified were most similar to Arochlor 1254. Dieldrin and DDT were the next most commonly detected pesticides. Aldrin and 2,4-D esters were detected in only a few samples. Lindane, toxophene, and

endrin were not detected in any of the sediment samples. Aldrin was found in only two of five samples collected at the Fall River site. The 2,4-D compounds were found in sediments from two of five sites in the Houston Ship Channel in Galveston Bay but were not found at any other location.

32. No significant correlations were detected between pesticide content and physicochemical parameters of the sediments, such as content of total organic carbon, oil and grease, and silt and clay fraction of the sediment. The pesticide content was more dependent on the quantity of pesticides used within the geographical region. Analyses of chlorinated hydrocarbon pesticides and PCB's in the interstitial water samples indicated the PCB's were present at all locations except Memphis. DDT was found only at the Chicago location; 2,4-D was found only in the Houston location; and dieldrin was found at the Memphis location.

33. There appeared to be no relationship between the concentration of pesticide in the sediment and the concentration of pesticides found in the interstitial or pore waters. Increasing sediment concentration did not result in increasing pore water concentration which further limits the mobility and acute bioavailability of PCB's. Also, there was no relationship between PCB content in the interstitial waters and the physicochemical parameters of the sediment such as total organic carbon, oil and grease content, silt and clay content. A high inverse relationship was found between PCB content in interstitial water and the TOC content of the interstitial water.

34. The most significant findings of this study were the apparent low concentrations of PCB's in the range of 0.15 ppb and DDT in the range of 0.15 ppb found in the pore waters. Such low concentrations indicate that during dredging operations, the release of the pore water and contaminants to the surrounding environment would not create environmental problems.

35. Analysis of chlorinated hydrocarbon pesticides and PCB's in the water column showed that there were no soluble pesticide materials found at the detection limits used (0.01 ppb). Pesticides that were

detected were associated with the suspended particulate matter. The range of total water concentrations (including soluble and suspended fractions) detected were 0.04 ppb of Arochlor 1242 and 0.004 ppb of dieldrin detected at Green Bay Wisconsin. Arochlor 1254 and dieldrin were detected in association with suspended materials from the water column in samples collected from the Tennessee Chute near Memphis, Tennessee. These strongly supported results indicate that chlorinated hydrocarbon pesticides and PCB's are rapidly sorbed from the aqueous solution and thus tend to be associated with suspended or sedimented material rather than in aqueous solution, significantly restricting their biological availability.

36. Analysis of the water at the sediment-water interface and the overlying water indicated that PCB's were found at all locations except at Fall River, Massachusetts. The concentrations of PCB's ranged from 0.01 ppb found at Green Bay to 0.08 ppb of Arochlor at Chicago.

37. Fulk et al. (1975) also evaluated the physical-chemical environmental factors that might affect release of pesticides. The following paragraphs summarize their findings.

38. a. Solids-to-liquid ratio. Apparently, a sediment-to-water ratio of greater than 1 to 4 or 1 to 5 was necessary before any release of chlorinated hydrocarbon pesticides occurred. The investigators did not check sediment ratios of greater than 1 to 4 or 1 to 5 because it was assumed that ratios higher than 1 to 4 or 1 to 5 would not occur during normal hydraulic dredging operations. No chlorinated hydrocarbons were detected in the soluble water phase in any of the mixture ratios below 1 to 4 or 1 to 5 indicating minimum release during dredging and disposal.

b. Effects of chlorinated hydrocarbon and PCB concentrations in sediments. The concentration of PCB's and chlorinated hydrocarbon pesticides in the sediment had a direct effect upon the quantity released. The relative amount released ranged from 1.8 percent of the total PCB concentration of the Houston sediment to 0.4 percent for the Memphis sediment. In summary, the ratio of solids to liquid and the concentrations of PCB's on the sediments affected the rate of release more than other factors.

c. Particle size and organic content of sediment. The effect of soluble organic carbon in the water is inversely proportional to the quantity of PCB's desorbed. Although no

PCB's were reported in the soluble fraction in the release studies, total PCB's were inversely related to the concentration of total organic carbon in the interstitial water. This would be assumed to be due to release occurring in the interstitial water. Release of pesticides was not related to particle size in this study.

- d. Oil and grease. The investigators were not able to arrive at conclusive results of the effects of oil and grease in sediments upon the release rates of PCB's or chlorinated hydrocarbons. It is somewhat difficult to obtain a water sample containing only soluble components since nonsoluble material removed by filtration will also often remove soluble components.
- e. Statistical analyses. Analysis of the data from release tests and settling tests indicated that 88 percent of the PCB variation between locations was related to variations in oil and grease content of the suspended sediments and the quantity of suspended solids in the water column. The analyses indicated that the oil concentration was about 20 times more important than quantity of suspended sediment in affecting the concentrations of PCB's in suspension.
- f. Summary. Fulk et al. (1975), indicated that the transfer of chlorinated hydrocarbons from bottom sediments to the soluble portion of the aqueous environment during dredging and disposal operations is not significant, especially at sediment-to-water ratios simulating dredging. However, sediment solids may remain in suspension and, thus, have a potential to effect the environment if there are significant quantities of pesticides on the suspended sediments. The major factors that apparently affect the concentration of PCB's or chlorinated hydrocarbons on the suspended sediments are oil and grease content of suspended sediments and previous opportunity for exposure to pesticides. The settling studies indicated that the concentration of pesticides associated with suspended solids returned to nearly normal after 24 hours of settling under quiescent conditions.

39. Work Unit 1C06. Chen et al. (1976), found DDT and homologs, dieldrin, and PCB's in sediments collected from the southern California area. They found that the concentration of both DDT and chlorinated hydrocarbons increased with increasing concentration of total organic carbon in the sediment. No soluble chlorinated hydrocarbons or oil and grease compounds were observed in the aqueous solutions due to the aquatic disposal of the dredged material. Most of the chlorinated hydrocarbons and oil and grease compounds were sorbed on suspended

materials. DDE generally accounted for 60 to 70 percent of the total chlorinated hydrocarbons in the sediment while PCB's constituted 10 to 20 percent of the total.

40. Summary. The chlorinated hydrocarbon content of sediments and the oil and grease content of sediments affect the solubility of chlorinated hydrocarbons in the aqueous environment. The amount of chlorinated hydrocarbons, PCB's, and oil and grease released into solution was insignificant. The major potential environmental impacts of disposing of contaminated sediments are from resuspension of sediments containing chlorinated hydrocarbons and PCB's adsorbed onto their surface. Resedimentation of pesticide-contaminated dredged material could have a potential impact on benthic organisms and delay recolonization of the new sediments.

41. The overall implications are:

- a. The concentration of PCB's and chlorinated hydrocarbons should be analyzed in every regional location as the concentration in the sediments appears to be strongly correlated to the historic use of pesticides within the area, total organic carbon content of the sediment, and oil and grease content of the sediment.
- b. At a sediment-to-water ratio of greater than 1:4, amounts of pesticides and PCB's may be released into the environment in association with suspended matter.
- c. Suspended material will usually settle within 24 hours in a quiescent area and form mounds of contaminated material with potential for benthic organism impact.

42. These findings indicate that the following operational guidelines should be considered to minimize possibly harmful effects of open-water disposal. If the concentration of PCB's and chlorinated hydrocarbon pesticides is high in the sediments, hydraulic pipeline dredging may result in their release in association with suspended material. The disposal site should be in a quiescent zone so that settling of suspended solids will occur as rapidly as possible and thus minimize the distribution of sediments.

#### Heavy metals

43. Aquatic environments, both freshwater and marine, achieve a balance between the influx of trace metals via natural sources and

deposition, complexation, and export to other systems. When man's activities change the balance by adding larger quantities of metals to the aquatic system through wastewater discharges, urban runoff, etc., a new balance has to be established. If the new balance tends to favor more sorption of the toxic metals by biological organisms, then either a short- or long-term deleterious effect may occur in this part of the ecosystem.

44. An important question is whether dredging and/or disposal operations shift equilibria or toxic metal balances enough to release biologically harmful concentrations of those heavy metals. If so, how long do the harmful levels persist and how much of the aquatic ecosystem is affected? The laboratory investigations synthesized herein define the boundary conditions or maximum and minimum conditions possible in the field; however, the final answers to these questions must be obtained by field studies and bioassay evaluations. These approaches and their findings are presented in three other synthesis reports (Brannon, 1978; Disalvo and Hirsch, 1978; and Wright, 1978).

45. Work Unit 1C03. Blom et al. (1976), studied the effects of sediment organic matter on the release of heavy metals and nutrients from both freshwater and saltwater sediments. No relationships were detected between the release of heavy metals into the overlying water and the concentration of total organic carbon of the water. This work showed that organic matter content of sediments was apparently not a general measure of the pollutive nature of dredged material or its ability to release contaminants.

46. Release of some heavy metals to the overlying water column was affected by the oxygen content of the sediments and overlying water. Greater release of metals occurred in oxygen-deficient waters, but the concentrations did not exceed ambient quality criteria for water, although a greater release trend appeared to exist in freshwater locations. Most of the heavy metals that occurred in the overlying water were associated with colloidal particulate material and had a lower bioavailability than solution forms.

47. The rate of release of manganese and cadmium from sediments to the overlying water column remained constant for the 4-month period

studied. Zinc, copper, chromium, nickel, and lead were released to the overlying water column initially, but the concentration decreased with time.

48. Significant quantities of all the heavy metals were released into the new interstitial waters of the resettled sediments, especially in fresh water. Although no relationship was observed between soluble organic carbon in the sediments and the rate of heavy metal release, it was felt that some specific organic compounds must have influenced the release of heavy metals. Two of the sediment samples contained high concentrations of petroleum hydrocarbons, and the release of heavy metals from these sediments was higher for some metals than in the other sediments.

49. The lack of conclusive interpretations in their study indicates the complexity involved in the chemistry of heavy metals and organic materials in sediments and natural waters. In general, there are two opposing interactions affecting desorption-adsorption of metals between the water and the particulate matter or sediments. First, in very anaerobic sediments containing high concentrations of sulfides, most of the heavy metals will exist as poorly soluble metal sulfides. Therefore, oxidation of anaerobic sediments would oxidize the sulfides and release the heavy metals. However, in oxidizing environments, soluble ferrous and manganous ions are oxidized and precipitate as hydrated metal oxides. The hydrated metal oxides adsorb other heavy metals from the aqueous solution and thus scavenge the heavy metals upon precipitation. The lack of clear release trends does, however, place special emphasis on benthic organisms that recolonize the newly formed sediment after a disposal operation.

50. Work Unit 1C05. Gambrell et al. (1977), found that the greatest release of iron and manganese was found in anaerobic environments (oxidation-reduction potentials between -150 and 0 mV) and at acid pH's (5 to 6). In very anaerobic sediments (oxidation-reduction potentials below -150 mV), most of the other heavy metals occurred as poorly soluble and usually somewhat stable forms, probably as sulfides. Under aerobic conditions (at oxidation-reduction potentials between +50 and

+500 mV with the highest potential representative of an upland or terrestrial environment, cadmium, mercury, and zinc were more soluble at an acid pH. At an alkaline pH, zinc and cadmium were not readily released under any aerobic conditions. Results of iron and manganese studies at acid and anaerobic conditions indicated that even in this anaerobic environment some oxidized form of iron existed. The investigators concluded that poorly crystalline hydrous oxides of iron and manganese were favored by two contrasting environments: one being a recently oxidized environment and the other a long-term anaerobic environment resulting in a lower potential for metal release.

51. It must be noted that anaerobic sediments have a stable neutral pH and that most natural waters are oxidized and neutral to alkaline in pH. Consequently, conditions that enhance release of iron, manganese, cadmium, mercury, and zinc do not normally occur at open-water disposal sites. These conditions can, however, exist in upland or terrestrial confined and unconfined disposal sites and offer the potential for release of these metals in what is generally considered the safest place for disposal of contaminated sediments. A thorough determination of the potential for change in the geochemical environment as well as other measures of pollution potential must be determined before selecting an open-water or upland disposal site.

52. Work Unit 1C06. Chen et al. (1976) found the release of toxic metals to the soluble phase to be ecologically insignificant. They did, however, show that certain sediments concentrated metals within themselves to potentially harmful levels. They also found that there is no correlation between releasable metals and total or bulk sediment concentrations and that oxidation-reduction reactions control release. Their data indicate that while some trace metals may be released in the parts-per-billion range or less, others show no release and most of the soluble concentrations are well below the allowable concentration levels of the ocean water discharge standards.

53. Summary. The results of these investigations are summarized as follows:

- a. Trace quantities of toxic heavy metals may be temporarily released if anaerobic sediments are discharged in well-

oxygenated waters. However, as the anaerobic forms of iron and manganese are oxidized, they will precipitate as hydrated oxides and scavenge most of the other trace heavy metals that might be released.

- b. Mercury, zinc, and cadmium may be released at potentially harmful levels if the sediments are highly contaminated with these metals and are placed in a well-oxidized, usually terrestrial, system.
- c. In addition to the effects that interactions of pH and oxidation-reduction potential have on the chemical forms of heavy metals in the sediments, specific organic compounds, which can chelate and complex heavy metals, determine the ability of heavy metals to dissolve or release into the water.

54. In general, unless sediments are highly contaminated with mercury, zinc, or cadmium, normal hydraulic dredging and open-water disposal should not release biologically significant quantities of toxic heavy metals for periods of more than a few hours. When such quantities were released initial concentrations were usually below water quality criteria for marine and freshwater systems.

55. One of the major factors in selecting the proper disposal site (i.e., well-mixed water, poorly mixed water, nearshore or upland) is an evaluation of the potential for change in the geochemical state of the disposal site. If the change in geochemical state is minor (i.e., disposal in well-mixed oxidized water with rapid settling to the bottom), potential for enhanced release of chemical constituents is minor. However, if placed on an upland terrestrial system where the sediments dry out to an arable soil material, the potential for release from highly contaminated sediments is greatest. These factors are discussed in much greater detail in the DMRP synthesis report (Gambrell et al., 1978) entitled "Disposal Alternatives for Contaminated Dredged Material as a Management Tool to Minimize Adverse Environmental Effects."

#### Nutrients

56. Nitrogen. Since most sediments are anaerobic at depths greater than just a few centimetres below the mud-water interface, most of the investigations of nitrogen constituents in sediments focused on ammonia.

57. Laboratory studies (Blom et al. 1976) showed that open-water disposal could release substantial quantities of ammonia. The quantity of ammonia released upon initial contact with the receiving water was positively related to the concentration of organic carbon and organic nitrogen in the sediments. Nitrification did occur in freshwater sediments dispersed in fresh water but not in freshwater sediments dispersed in sea water. It was concluded that nitrifying bacteria acclimated to freshwater sediments were not able to rapidly acclimate to the sea water environment.

58. Gambrell et al. (1977) found that both pH and oxidation-reduction potential influenced the quantity of ammonia that might be released from the sediments. Highest amounts of ammonia were released to the overlying water column from sediments with low pH (5 to 6) and lowest oxidation-reduction potential (-150 mV). At pH's of 7 to 8, some of the ammonia was apparently lost to the atmosphere.

59. These two laboratory investigations confirmed results published by other investigators. In general, anaerobic sediments may contain elevated concentrations of ammonia formed from bacterial degradation of organic nitrogen. Dredging and open-water disposal can release potentially lethal levels of ammonia from the dredged material, especially from the interstitial waters. If the receiving water at the disposal site has adequate dissolved oxygen, bacteria may convert the ammonia to nitrate. However this process may take several days depending on the physical-chemical conditions and presence of acclimated nitrifying bacteria. Dilution would be most important in decreasing concentration of ammonia below toxic levels.

60. Chen et al. (1976) noted that nutrient release was found to be in the subparts-per-million to parts-per-million ranges, which may increase the productivity of open waters. In a restricted area with little circulation and dilution, ammonia can be released to toxic levels exceeding 10 ppm under prolonged contact of sediment with anaerobic overlying waters. Under oxidizing conditions, nitrogen compounds increased during the beginning contact period (about 1 to 2 months) then decreased. Ammonia decreased to zero due to oxidation to nitrate.

61. The significance of the results for dredging and open-water disposal operations is that open-water disposal can cause release of lethal levels of ammonia for hours or less. Therefore, ammonia concentrations should be monitored at open-water disposal sites and the disposal operations should be carefully reviewed if excessive levels occur.

62. Phosphorus. Blom et al. (1976) found only low-level releases of ortho-phosphate from most sediments. An exception was sediment that contained elevated levels of petroleum-type compounds. Highest concentrations of phosphorus were found in the water column immediately after disposal. Apparently the soluble phosphorus was released from the sediment interstitial waters. The amount of phosphorus in aqueous solution rapidly declined to insignificant levels (in a matter of minutes) due to sorption by iron hydrous oxide colloidal particles.

63. Gambrell et al. (1977) found the highest concentrations of soluble phosphorus occurred in anaerobic sediments (oxidation-reduction potential of -150 mV) and at pH 6.5. More acidic (i.e., pH 5) or alkaline conditions (i.e., pH 8.0) decreased levels of soluble phosphorus in sediments. However, in more oxidized suspensions (250 to 500 mV oxidation-reduction potential), an increase in pH from 5.0 to 8.0 resulted in an increase in soluble phosphorus.

64. Chen et al. (1976) found releases of phosphorus in the subparts-per-million to parts-per-million levels that were related to oxidation-reduction conditions. Under anaerobic conditions, the release mechanism for phosphorus was the same as for oxidizing conditions, but generally with higher release rates.

65. Therefore, open-water disposal of dredged material containing elevated levels of phosphorus can result in the release of soluble phosphorus to the receiving body of water. The soluble phosphorus will be scavenged from the water column by sorption on iron hydrous oxide particles. Also, soluble phosphorus is rapidly sorbed by microbial organisms and primary producers such as algae and diatoms. Thus, the short-term releases of low levels of phosphorus from open-water disposal of dredged material can stimulate growth of primary producers in the receiving environment. The potential impact of the stimulation

would have to be compared to the overall ecological balance and aesthetics of the receiving environment. Open-water disposal of phosphate-containing dredged material containing mobile and available forms of phosphorus should be carefully reviewed when the receiving environment is already subject to periodic blooms of nuisance algae.

#### PART IV: CONCLUSIONS

66. Published literature and results of DMRP research reviewed in this synthesis report indicate that open-water disposal of dredged material can have a temporary impact upon the receiving aqueous environment if the dredged sediments contain elevated levels of chlorinated pesticides, PCB's, or ammonia. Harmful levels of heavy metals can be released from sediments at certain combinations of pH and oxidation-reduction potential but probably would not be released by most typical dredging or disposal operations. Chlorinated hydrocarbon pesticides, PCB's, oil and grease compounds, heavy metals, and phosphates are rapidly sorbed by suspended particulate material in the water column that may resediment in quiescent areas.

67. Resedimentation of suspended particles that have sorbed any of the above contaminants creates a potential for impact upon benthic organisms. After colonization occurs, detrital-feeding organisms may accumulate pesticides, PCB's, oil and grease compounds, and heavy metals and thus introduce these constituents into the biological food chain. These effects were reviewed and synthesized by Disalvo and Hirsch (1978).

68. Most of the results reviewed in this report were concerned with short-term effects of constituents associated with sediments. Long-term (one year or more) effects due to open-water disposal of dredged material may occur but cannot be predicted at this time. Such effects may become apparent from DMRP field studies and will be addressed in the DMRP Task 1A synthesis report (Wright, 1978).

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## APPENDIX A: METHODS SUMMARY

1. Presented for general information only is a summary of experimental designs, methodologies, and analytical methods employed in the DMRP Task 1C research investigations. For a more rigorous treatment of the experiments and for application in future projects, the reader is referred to the DMRP contract reports for Work Units 1C03 (Blom et al. 1976), 1C04 (Fulk et al., 1975), 1C05 (Gambrell et al., 1977), and 1C06 (Chen et al., 1976).

### General Fractionation Procedures

2. All of the investigators fractionated constituents from the sediment samples into interstitial water, suspended or colloidal fractions, and total water-soluble fractions using the scheme shown in Figure A1 and employed the analytical methods presented in Table A1.

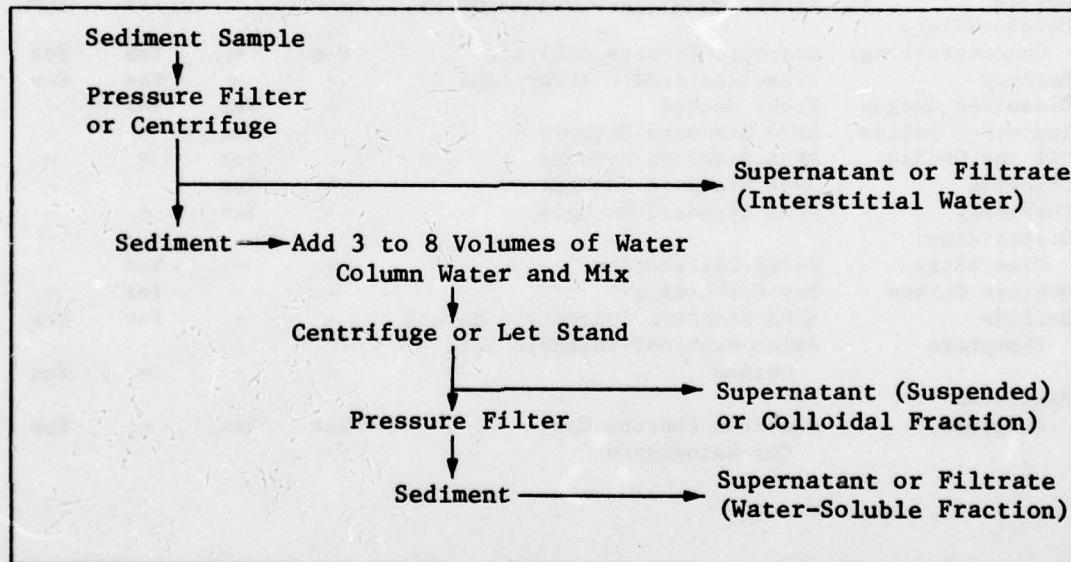


Figure A1. Generalized flow diagram of sediment fractionation procedure

Table A1  
Analytical Methods Used by Task 1C Work Unit Investigators

Parameter	Method of Analysis	Work Units			
		1C03	1C04	1C05	1C06
pH	Probe	Yes	Yes	Yes	Yes
Eh (oxidation-reduction)	Platinum Electrode	Yes	Yes	Yes	-
COD	APHA Standard Methods	Yes	-	-	-
NH3 -N	Ammonia Specific Ion Electrode	Yes	-	-	-
NO3 -N	APHA Standard Methods	Yes	-	-	-
PO4	APHA Standard Colorimetric Methods	Yes	-	Yes	-
Iron	APHA Standard Methods or Hach Colorimeter	Yes	-	-	-
Alkalinity	APHA Standard Methods-Titrimetry	Yes	-	-	-
Conductivity	YSI conductivity Meter	Yes	-	-	-
Total Organic Carbon	Total Organic Carbon Analyzer	Yes	Yes	-	-
Anodic Stripping Voltammetry	Princeton Applied Research Polarographic Cell and Chemtrix SSP-5A Polarograph with Storage Oscilloscope	Yes	-	-	-
Metals	Atomic Absorption Spectrometry	Yes	-	Yes	Yes
Metals (Trace Concentrations)	Graphite Furnace Analyzer	Yes	-	Yes	Yes
Mercury	Flameless Atomic Absorption	-	-	Yes	Yes
Dissolved Oxygen	Probe Method	-	Yes	Yes	-
Suspended Solids	APHA Standard Methods	-	Yes	-	-
Oil and Grease	APHA Standard Methods	-	Yes	-	-
Chloride	APHA Standard Methods	-	Yes	-	-
Turbidity	APHA Standard Methods	-	Yes	-	-
Crystalline Mineralogy	X-Ray Diffraction	-	-	Yes	-
Organic Carbon	Dry Combustion	-	-	Yes	-
Sulfide	APHA Standard Iodometric Method	-	-	Yes	Yes
Phosphate	Amino-Naphthol-Sulfuric Acid Method	-	-	-	Yes
Pesticide Analyses	Electron Capture Gas Chromatography	Yes	Yes	-	Yes

The procedures were designed to duplicate field conditions as closely as possible in laboratory studies. Sediment core samples were stored under oxygen-free conditions by displacing air above the sediment samples with nitrogen gas. Some minimal oxidation of the surface of the sediment cores probably occurred before the samples were stored in the oxygen-free containers. However, the amount of oxidation did not invalidate the laboratory analyses. Sediments would probably be partially oxidized during dredging operations and subsequent disposal of the dredged material.

#### Specific Procedures

3. In addition to the generalized fractionation procedure used by all of the investigators, selected specific fractions of the sediment constituents were obtained by the different contractors as discussed in the following sections on each work unit.

##### Work Unit 1C03

4. The major objective of this investigation was to evaluate the effect of organic matter in sediments upon the release or migration of trace metals and nutrients. Sediment core samples were collected from three estuarine sites in the Hudson and Passaic Rivers near New York City, New York, and from three freshwater sites near Detroit, Michigan, (Table 1). Sediment samples in core tubes were packed in ice and air freighted to the laboratory. Sediment samples were composited within three days after collection and stored under nitrogen environments for periods up to one month prior to fractionation of chemical constituents.

5. The sediment chemical constituents were separated into interstitial, colloidal or suspended, and water soluble components (Figure A1). The fate of suspended and soluble components during a one- to two-month settling period was also evaluated. The sediment was mixed with either fresh or salt water collected from the same site as the sediment and allowed to settle under test conditions of  $10^{\circ}\text{C}$ , in the dark at 4 to 6 mg/l dissolved oxygen concentration in the water.

6. Organic acids were extracted from the aqueous phases with acetone and separated into a humic acid fraction by dialysis and a fulvic acid fraction by passage through a strong acid cation exchange resin in the H<sup>+</sup> form.

7. Organic acids were analyzed by infrared and ultraviolet spectrophotometry. Molecular weights of the acid fractions were determined by gel permeation and ultrafiltration techniques. Anodic stripping voltammetry was used for determining the concentrations of uncomplexed metal ions. All other analyses were performed according to the American Public Health Association (APHA) Standard Methods (1965) or the best method available (Table A1).

Work Unit 1C04

8. The major objective of this study was to determine the extent of pesticide and PCB release from sediments. Water and sediment samples were collected from three freshwater sites and two estuarine sites (Table 1). Water column samples were collected 0.5 m from the bottom, middepth, and 0.5 m from the surface with a Kemmerer water sampler. Interfacial samples were collected from 0.6 to 1.3 cm above the bottom in a specially constructed sampler. All water samples were stored in glass containers with aluminum foil or Teflon liners in the caps. Samples were iced down and air freighted to the laboratory within 24 to 48 hours.

9. Sediment samples were collected by forcing acrylic plastic tubes into the bottom. Tubes were rubber stoppered and stored on ice. An interstitial water fraction was obtained by centrifuging the wet composited sediment samples at 1,000 times gravity initially and then at 10,000 times gravity to remove very fine particles. Composited sediment samples were mixed with four volumes of water column water for two minutes and then allowed to settle. The supernatant water which should have contained suspended and soluble constituents, was analyzed as the so-called "settling test" fraction. An equilibrium fraction was obtained by mixing the composited sediment sample with water column water for 24 hours. After mixing, sediments and suspended materials were removed by centrifuging at 1,000 times gravity initially and then at 10,000 times gravity.

10. The interstitial water, supernatant waters from the settling and equilibrium tests, and water column water from the original collection site were analyzed for pesticides and PCB's by procedures prescribed for National Pollutant Discharge Elimination System (NPDES) (Lotse et al., 1968). Other analyses were performed by the APHA Standard Methods (Table A1).

11. Analyses for oil and grease, total organic carbon, pH, solids, chloride, and turbidity were performed in accordance with either the EPA Manual for Chemical Analysis of Water and Wastes (EPA, 1971), or APHA Standard Methods (APHA, 1965) (Table A1). Pesticide analyses were performed by solvent extraction and gas chromatography of the "cleaned-up" extracts.

Work Unit 1C05

12. The objective of this study was to determine what effect pH and oxidation-reduction potential had upon release of chemical constituents from sediments. Sediment samples were collected with a Peterson dredge from two estuarine and two freshwater areas along the Gulf of Mexico coastline (Table 1). The sediments were composited and stored in a nitrogen atmosphere at 4°C until analyzed.

13. Centrifugation and chemical extractions were conducted under a nitrogen atmosphere to inhibit oxidation of heavy metals in the sediments. Total metals of the sediments were analyzed after sequential digestion with concentrated nitric, hydrochloric, and perchloric acids. The digested sediments were then dissolved with hot concentrated hydrochloric and diluted to 50 ml. The sediments were incubated with surface water samples in the specially designed chamber to control oxidation-reduction potential by addition of nitrogen gas or air and using natural microbial processes to poise the oxidation-reduction potential at the desired level. Sediment-water samples were incubated at specific pH and redox potentials for 9 to 11 days before being fractionated.

14. In addition to the interstitial, suspended or colloidal, and water-soluble constituents (Figure A1), selected fractions were obtained from the sediments by special extraction procedures (Figure A2). The specific extraction and incubation procedures were designed to determine

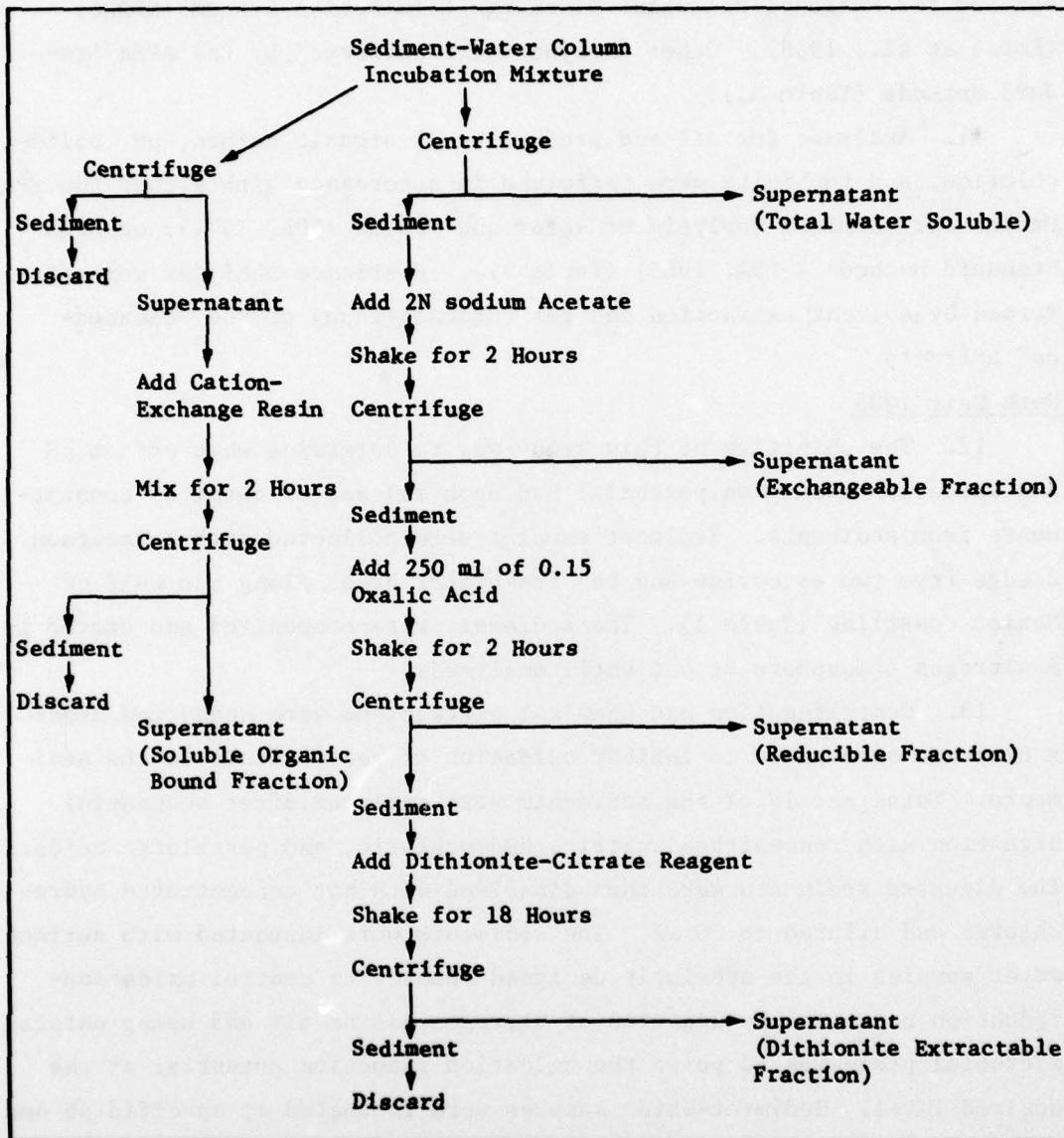


Figure A2. Fractionation procedure used by Gambrell et al. (1977) to obtain specific sediment-water fractions

the effects of pH and oxidation-reduction potential upon the release mechanisms of the chemical constituents from the sediments.

15. Metals concentration in each fraction was analyzed by atomic absorption-graphite furnace spectrophotometer. Matrix interferences were reduced by addition of 5 percent  $\text{NH}_4\text{NO}_3$  in the graphite furnace and corrected for by the method of standard additions. Other analyses were performed by standard methods (Table A1).

Work Unit 1C06

16. The objective of this investigation was to determine the effect of dispersion, settling, and resedimentation on migration of chemical constituents during open-water disposal of dredged materials. Sediment samples were collected by box core and grab samplers from an estuarine site and a freshwater site in California (Table 1). Sediment samples were stored in a nitrogen atmosphere at  $4^{\circ}\text{C}$  until analyzed.

17. Interstitial water and water-soluble fractions were removed from the composited sediment samples by pressure filtration in a nitrogen atmosphere (Figure A1). In addition, an ammonium acetate solution in a 1:6 (solids:liquid) ratio was mixed for 90 minutes with the sediments to determine the quantity of exchangeable chemical constituents. Other fractions extracted were the acetic acid phase, easily reducible phase, organic and sulfide phases, moderately reducible phase, and the residual (lithogenous fraction) phase.

18. An experiment was performed to determine the migration of constituents from sediments into the water column by mixing sediments with water column water in a 5-ft-tall plexiglass cylinder. The water column water was agitated with either compressed air to simulate an oxygen-rich environment or with nitrogen gas to simulate an oxygen-free environment. Samples of the water column water and suspended sediment were fractionated by the previously described procedure.

19. Long-term experiments were performed to determine the effects of disturbed sediments that were not allowed to resettle and disturbed sediments that were allowed to resettle in the water column. The tests were performed in a dark temperature chamber at oxygen-rich, low-oxygen, and oxygen-free conditions.

20. Total metals concentration in the fractions was determined by an atomic absorption spectrophotometer equipped with a heated graphite atomizer (HGA). Chromium, iron, and manganese were analyzed by direct injection on the HGA. Silver, cadmium, copper, nickel, lead, and zinc were chelated and extracted from the aqueous phases with ammonium pyridine dithiocarbamate (APDC) and methyl isobutyl ketone (MIBK) prior to injection. Mercury was analyzed by flameless atomic absorption spectrophotometry. Chlorinated hydrocarbon pesticides were extracted and analyzed by reconized procedures (Armour and Burke, 1970). All other analyses were performed by APHA (1965) or EPA (1971) standard methods (Table A1).

In accordance with letter from DAEN-RDC, DAEN-ASI dated 22 July 1977, Subject: Facsimile Catalog Cards for Laboratory Technical Publications, a facsimile catalog card in Library of Congress MARC format is reproduced below.

Burks, Sterling A

Water quality impacts of aquatic dredged material disposal (laboratory investigations) / by Sterling A. Burks and Robert M. Engler]. Vicksburg, Miss. : U. S. Waterways Experiment Station ; Springfield, Va. : available from National Technical Information Service, 1978.

35, 8 p. : ill. ; 27 cm. (Technical report - U. S. Army Engineer Waterways Experiment Station ; DS-78-4)

Prepared for Office, Chief of Engineers, U. S. Army, Washington, D. C.

Literature cited: p. 32-35.

1. Aquatic environment. 2. Bottom sediment. 3. Contaminants.
4. Dredged material. 5. Dredged material disposal.
6. Pollutants. 7. Waste disposal sites. 8. Water pollution.
9. Water quality. I. Engler, Robert M., joint author.
- II. United States. Army. Corps of Engineers. III. United States. Waterways Experiment Station, Vicksburg, Miss.

Technical report ; DS-78-4.

TA7.W34 no.DS-78-4